

# KINETICS MODELING OF THE ATMOSPHERIC-PRESSURE CHEMICAL VAPOR DEPOSITION OF SILICON DIOXIDE FROM SILANE AND OXYGEN

Carmen J. Giunta  
Department of Chemistry  
Le Moyne College  
Syracuse, NY 13214-1399

Keywords: kinetics model, oxidation, silane

## Abstract

The oxidation of  $\text{SiH}_4$  by  $\text{O}_2$  is a reaction of interest to chemists in the areas of both combustion and chemical vapor deposition. A detailed kinetics model of this reaction, developed to explain combustion data,<sup>1</sup> is applied with slight modification to kinetic data from atmospheric-pressure thermal chemical vapor deposition (CVD) of  $\text{SiO}_2$  films.<sup>2</sup> The model is also compared to a  $\text{CH}_4$  oxidation model under the same CVD conditions, to elucidate differences in the oxidation of  $\text{SiH}_4$  and  $\text{CH}_4$  under mild conditions. A key difference stems from the rates and major products of the reaction of  $\text{O}_2$  with  $\text{SiH}_3$  vs.  $\text{CH}_3$  radicals.

## Introduction

The first serious attempt to model the kinetics of the oxidation of silane by oxygen came from the combustion chemistry community,<sup>3</sup> as well as the most comprehensive effort to date (hereafter called BTW after its authors' initials)<sup>1</sup>. Meanwhile, materials scientists, electronics engineers, and others have been interested for over 25 years in a controlled version of silane oxidation under mild conditions, an example of the now widely used technique of chemical vapor deposition (CVD).<sup>4</sup> The interest of this latter group stems from the fact that this reaction can produce thin films of  $\text{SiO}_2$ , useful for a variety of purposes in the semiconductor industry and elsewhere.

This paper focuses on a report of the film growth kinetics of such a CVD process, a report rich in kinetic information (deposition rates as a function of distance along the gas flow in the reactor under a variety of concentrations and temperatures) obtained under relatively simple conditions of fluid flow (laminar flow between parallel plates).<sup>2</sup> The report (hereafter called EH after its authors' initials) is a source of data amenable to modeling, and I attempted to model that data using the BTW mechanism with only slight modification. The conditions employed by EH (atmospheric pressure, low  $\text{SiH}_4/\text{O}_2$  ratios, mild reaction) are sufficiently different from those for which the BTW mechanism was developed (ignition data over a range of pressures) as to test the robustness of the BTW mechanism.

The questions I addressed are: Can the BTW mechanism adequately model the EH data? How should the mechanism be modified? What are the principal pathways of the mechanism under the conditions employed by EH? How do these pathways differ from those of methane oxidation?

## Computational Method

Model growth profiles were obtained by numerically integrating the applicable differential equations for reaction and diffusion in two dimensions. The equations describing reaction in the  $\text{SiH}_4/\text{O}_2$  system were the mass-action rate equations defined by the 70 reversible elementary reactions among 23 species listed by BTW in their Table I. (I use their numbering in referring to reactions below.) For comparison, the  $\text{CH}_4/\text{O}_2$  system was represented by 73 reactions total among 19 species. This reaction list is the  $\text{CH}_4/\text{O}_2$  subset of a mechanism developed to model the CVD of  $\text{SnO}_2$  from  $(\text{CH}_3)_4\text{Sn}$  and  $\text{O}_2$ .<sup>5</sup> The  $y$  dimension is normal to both the flow and the substrate in the horizontal, laminar-flow reactor; the  $x$  direction is along the flow, and it represents the temporal evolution of the reaction. Inclusion of the  $y$  dimension permitted explicit consideration of the large temperature gradients present in the reactor along that dimension, by allowing for spatially varying rate coefficients. It also facilitated treatment of diffusion normal to the substrate, and direct evaluation of the deposition rate from the diffusive flux onto the growth surface of species which stick to the surface. Details on the computational methods are reported elsewhere.<sup>6</sup>

## Results and Discussion

### Can the BTW mechanism adequately model the EH data?

The maximum deposition rate in the profiles reported by EH is rather weakly dependent on the temperature of the hot substrate, as shown in Fig. 1; the activation energy is about  $27 \text{ kJ mol}^{-1}$  over the range 742-845 K. The maximum film growth rate is weakly but inversely dependent on initial oxygen mixing ratio (always in large excess), as illustrated in Fig. 2. And the maximum growth rate is strongly dependent on initial silane mixing ratio, as shown in Fig. 3. If the data (only three data points) define a power-law dependence, the order with respect to silane is around 1.34. Increasing the flow rate pushes the position of the maximum deposition rate downstream and spreads it out, without greatly altering the shape of the profile. Increasing the temperature of the cool wall of the reactor increases the maximum deposition rate only slightly, and does not otherwise alter the shape of the deposition profile.<sup>2</sup>

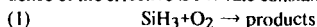
The BTW mechanism led to model deposition profiles which reproduce all of the above trends, albeit with higher deposition rates and earlier deposition maxima (discussed below). The activation energy of the maximum deposition rate in the model was about  $29 \text{ kJ mol}^{-1}$  over the range 742-845 K, as shown in Fig. 1. The peak deposition rate declined slightly but noticeably upon increasing the oxygen mixing ratio from 1.7% to 25%, as illustrated in Fig. 2, although this

inverse relationship seemed to bottom out thereafter. The peak deposition rate followed a power law of order 1.46 with respect to initial silane mixing ratio, as illustrated in Fig. 3. Doubling the flow rate doubled the downstream position of the growth maximum and practically doubled the width of the deposition profile. Increasing the temperature of the cold wall had virtually no effect on the model profile.

Despite the success of the BTW model in capturing the qualitative trends described above, the deposition profiles produced by my model simulations did not greatly resemble the profiles published by EH. (See Fig. 2, which illustrates one of the better resemblances between model and experiment!) In particular, the model profiles peaked too early and too high. To understand this discrepancy, it is necessary to note that in all the model simulations presented here, the temperature was taken to be constant along the  $x$  (flow) direction. That is, the short space needed for the gases to warm up to the reactor temperature was neglected. This simplifying assumption facilitated a substantial savings in computational effort and time, and significantly enhanced the numerical tractability of the model's differential equations. However, it also altered the position and magnitude of the maximum deposition rate from what the model would predict if the development of the temperature field had been treated explicitly. The model deposition profiles presented here put the maximum deposition rate very close to the reactor inlet, certainly within the warm-up zone. My experience with modeling another rapid oxidation of silanes<sup>6b</sup> suggests that treating the transient temperature field explicitly would delay the deposition maximum until the end of the warm-up zone, and spread out the deposition profile somewhat, concomitantly lowering the maximum deposition rate by some 30%. Therefore, the profiles presented here can be expected to have their deposition maxima pushed about 1 cm downstream, spread out, and lowered. These changes would bring the model profiles into much better agreement with the experimental data reported by EH. But a rigorous and quantitative comparison must await simulations in which the development of the temperature field along the flow direction is explicitly treated.

**How should the mechanism be modified?**

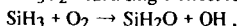
From the viewpoint of reproducing the experimental data, the model profiles should be modified to reduce the deposition peak and move it downstream. That, I expect, will occur with careful treatment of the early temperature field. Still, I considered the BTW mechanism flawed in its treatment of the reaction of the  $\text{SiH}_3$  radical with  $\text{O}_2$ . The BTW mechanism includes several product channels for this reaction, all proceeding through an excited adduct " $\text{xSiH}_3\text{O}_2$ ", which is included explicitly in the mechanism. First, the rate constant assigned to formation of the adduct (R16 reverse) is two orders of magnitude greater than gas kinetic. Second, the temperature dependence of the effective BTW rate constant for the overall reaction



appears to contradict the only published data on the subject.<sup>7</sup>

The first objection was easily remedied. Running the model with the rate constants for R16 and its reverse reaction decreased by a factor of 100 had no effect on the model deposition profiles. In fact, decreasing the rate constants by a further factor of 50 had a negligible effect. Thus, the BTW model results described above were not limited by the value of the rate constant for formation of the excited adduct  $\text{xSiH}_3\text{O}_2$ .

The second objection, however, was not so easily resolved. Slagle et al. report a small negative activation energy for reaction (1) over 296-500 K, whereas the effective activation energy in the BTW mechanism is positive over the same range. I tried replacing all the BTW reactions involving excited  $\text{xSiH}_3\text{O}_2$  with a single direct reaction

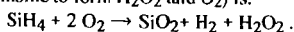


and I assigned to this reaction the rate constant reported by Slagle et al. The resulting model profiles differed negligibly from those discussed above. Thus, not surprisingly, the excited  $\text{xSiH}_3\text{O}_2$  (when it was left in the mechanism) functioned as a flow-through species, at least under the modeled conditions. But making  $\text{SiH}_2\text{O} + \text{OH}$  the dominant products of reaction (1) is at odds with reports by Koshi et al. that  $\text{HSiOOH} + \text{H}$  are the major products (at least at room temperature and 5 Torr).<sup>8</sup> The BTW mechanism is actually consistent with the product branching ratio reported by Koshi et al., because it assigns a different temperature dependence to the product channels  $\text{HSiOOH} + \text{H}$  (R59) and  $\text{SiH}_2\text{O} + \text{OH}$  (R60). Thus, the BTW mechanism says that  $\text{HSiOOH} + \text{H}$  is the main channel at room temperature but  $\text{SiH}_2\text{O} + \text{OH}$  at elevated temperatures; but that temperature dependence conflicts with Slagle et al. The problem is that the model only reproduced the EH data well if  $\text{SiH}_2\text{O} + \text{OH}$  was the dominant channel. Yet it did not appear possible to construct rate constant expressions consistent with both Slagle et al. and Koshi et al. that also make  $\text{SiH}_2\text{O} + \text{OH}$  the dominant channel at the temperatures employed by EH.

**What are the principal pathways of the mechanism?**

Model output included concentration profiles for every species. Thus, it was possible to analyze the output to determine which reaction or reactions were primarily responsible for producing and consuming each species. Piecing together these primary pathways allowed me to construct a simplified route from  $\text{SiH}_4$  via several intermediates to the deposited film. This scheme for the BTW model under EH conditions is shown in Fig. 4.

The scheme amounts to a branching chain reaction propagated by OH and  $\text{SiH}_3$ .  $\text{SiH}_4$  was primarily destroyed by OH in a hydrogen abstraction reaction (reaction R13). The resulting  $\text{SiH}_3$  radical reacted with  $\text{O}_2$  via the flow-through intermediate  $\text{xSiH}_3\text{O}_2$  to regenerate OH and produce  $\text{SiH}_2\text{O}$  (R16 reverse).  $\text{SiH}_2\text{O}$  in turn reacted with  $\text{H}_2\text{O}$  produced from reaction R13 above, yielding  $\text{HSiOOH}$  and  $\text{H}_2$  (R62). Successive removal from  $\text{HSiOOH}$  of the remaining H atoms by reactions with  $\text{O}_2$  (R65 and R67) produced  $\text{SiO}_2$ , the main film depositing species.\* The overall reaction stoichiometry implied by this sequence (assuming that the  $\text{HO}_2$  radicals formed in reactions R65 and R67 combine to form  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ ) is:



But in the model, the  $\text{HO}_2$  radicals also provide some branching, for some of them can go back to abstract hydrogen from  $\text{SiH}_4$  (R15).

This reduced reaction set (including HO<sub>2</sub> self-reaction, and supplemented by

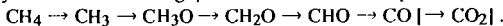
(R23)  $\text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2$   
to initiate production of reactive intermediates and by

(R11 reverse)  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$

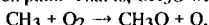
to include all the important reactions controlling OH concentration) was sufficient to capture the main features of the modeled growth profiles presented above. The dependence of the maximum growth rate on both the substrate temperature and the cool wall temperature is small. Its dependence on initial oxygen concentration is small (although, unlike the full model and experiment, positive). And its dependence on initial silane concentration is close to 1.5 order.

**How do these pathways differ from those of methane oxidation?**

In one sense, comparing principal pathways of methane oxidation and silane oxidation is a bit like comparing apples and oranges, for the two oxidations occur under different conditions. For example, under the concentration and temperature conditions employed by EH, methane oxidation essentially does not occur. To simulate methane depletion comparable to the modeled silane depletion under conditions of identical reactant concentrations, flow velocity, and temperature gradient, a substrate temperature nearly 300 degrees greater was necessary. Under such conditions the main pathway for carbon-containing species was the familiar sequence:

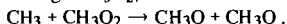


(The final product was a mixture of CO and CO<sub>2</sub>.) At these temperatures, CH<sub>3</sub> association with O<sub>2</sub> to reversibly form CH<sub>3</sub>O<sub>2</sub> was important to the CH<sub>3</sub> budget, but it was essentially a detour from the oxidation path. That is, CH<sub>3</sub>O was produced mainly by

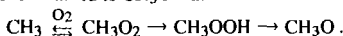


rather than in a pathway leading through CH<sub>3</sub>O<sub>2</sub>, such as decomposition of CH<sub>3</sub>OOH.

Perhaps a more interesting comparison is to examine the oxidation of *methyl* under CVD conditions. Modeling CH<sub>3</sub> oxidation at these lower temperatures showed a different oxidative pathway for CH<sub>3</sub>. Here CH<sub>3</sub> rapidly and reversibly associated with O<sub>2</sub>, and the path to further oxidation passed through CH<sub>3</sub>O<sub>2</sub>, via



Of course generating initial CH<sub>3</sub> concentrations equal to the initial SiH<sub>4</sub> concentrations employed by EH under such mild conditions is unrealistic. Still, the importance of CH<sub>3</sub>O<sub>2</sub> to methyl oxidation illustrated in this hypothetical case was also seen in the simulations of ref. 5a, in which much smaller CH<sub>3</sub> concentrations arose from decomposition of (CH<sub>3</sub>)<sub>4</sub>Sn under CVD conditions. In ref. 5a, the sequence that led to CH<sub>3</sub>O was:



Both here and in ref. 5a, the relatively low temperature and substantial pressure favored the associative channel in the reaction between CH<sub>3</sub> and O<sub>2</sub> so much that the chain-branching, oxygen-splitting channel to CH<sub>3</sub>O was only a minor, even negligible, producer of CH<sub>3</sub>O.

In contrast, neither SiH<sub>3</sub>O nor a stabilized SiH<sub>3</sub>O<sub>2</sub> played an important role in the fate of SiH<sub>3</sub> in the BTW mechanism under EH conditions or in direct studies of reaction (1). Several groups have reported that reaction (1) exhibits no pressure dependence, at least at the low pressures (less than 27 Torr) studied; they interpret this pressure independence as evidence that formation of a stabilized SiH<sub>3</sub>O<sub>2</sub> product is negligible.<sup>7,9</sup> While it is quite conceivable that formation of SiH<sub>3</sub>O<sub>2</sub> is negligible at 27 Torr and significant at atmospheric pressure, modeling evidence suggests that this is not the case. I varied the rate constant for SiH<sub>3</sub>O<sub>2</sub> formation, and found that when it was a significant channel of the reaction (1), the activation energy of the peak deposition rate was much higher than observed by EH. If SiH<sub>3</sub>O<sub>2</sub> played an important role, its decomposition (R36) with a substantial activation energy would contribute to the formation of SiH<sub>2</sub>O and subsequent steps on the path to film deposition. Reaction (1) is clearly an important step in silane oxidation, and further study of it is needed, particularly at atmospheric pressure and elevated temperatures.

## Conclusion

The BTW mechanism qualitatively reproduced trends observed by EH in the CVD of SiO<sub>2</sub> from SiH<sub>4</sub> and O<sub>2</sub> with respect to temperature, reactant concentration, and flow velocity. A rigorous quantitative comparison of modeled growth profiles to experimental ones must await explicit treatment of the transient temperature field near the reactor inlet. The ability of the BTW mechanism to model CVD data was not lost by changing its rate of SiH<sub>3</sub> association with O<sub>2</sub> to form a flow-through xSiH<sub>3</sub>O<sub>2</sub>, provided that SiH<sub>2</sub>O + OH is the ultimate product of the encounter. The reaction of SiH<sub>3</sub> with O<sub>2</sub> is an important step in silane oxidation, and one which differentiates silane oxidation from methane oxidation. The BTW model was consistent with much but not all the available data on the SiH<sub>3</sub> + O<sub>2</sub> reaction.

## References

- <sup>1</sup>Britten, J. A.; Tong, J.; Westbrook, C. K. *Symp. (Int.) Combust., [Proc.]*, 23rd 1990, 195.
- <sup>2</sup>Ellis, F. B., Jr.; Houghton, J. *J. Mater. Res.* 1989, 4, 863.
- <sup>3</sup>Jachimowski, C. J.; McLain, A. G. NASA Technical Paper 2129: "A chemical kinetic mechanism for the ignition of silane/hydrogen mixtures", 1983.
- <sup>4</sup>Goldsmith, N.; Kern, W. *RCA Rev.* 1967, 28, 153.
- <sup>5a</sup>Zawadzki, A. G.; Giunta, C. J.; Gordon, R. G. *J. Phys. Chem.* 1992, 96, 5369; <sup>b</sup>Giunta, C. J.; Strickler, D. A.; Gordon, R. G. *J. Phys. Chem.* 1993, 97, 2275. The reactions are listed explicitly under the headings "Hydrogen Oxidation Reactions" and "Hydrocarbon Oxidation Reactions" in Table I of ref. 5b.
- <sup>6a</sup>Giunta, C. J.; Chapple-Sokol, J. D.; Gordon, R. G. *J. Electrochem. Soc.* 1990, 137, 3237; <sup>b</sup>Giunta, C. J. Ph.D. Thesis, Harvard University, 1989.
- <sup>7</sup>Slagle, I. R.; Bernhardt, J. R.; Gutman, D. *Chem. Phys. Lett.* 1988, 149, 180.

- <sup>8a)</sup>Koshi, M.; Miyoshi, A.; Matsui, H. *J. Phys. Chem.* **1991**, *95*, 9869; <sup>b)</sup>Koshi, M.; Nishida, N.; Murakami, Y.; Matsui, H. *J. Phys. Chem.* **1993**, *97*, 4473.
- \*My implementation of the model allowed SiO<sub>2</sub> as well as every silicon-containing reactive intermediate to deposit if it diffused to the surface. Any partially oxidized silicon intermediates that deposited were assumed to undergo rapid subsequent reaction on the surface to yield SiO<sub>2</sub> film. Unoxidized intermediates like SiH<sub>2</sub> and SiH<sub>3</sub> that deposited were assumed to yield silicon film. Thus, it is not tautologous to state that SiO<sub>2</sub> was the principal depositing species. SiOOH also contributed substantially to the modeled deposit.
- <sup>9a)</sup>Chasovnikov, S. A.; Krasnoperov, L. N. *Khim. Fiz.* **1987**, *6*, 956; <sup>b)</sup>Sugawara, K.; Nakanaga, T.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* **1989**, *157*, 309.

## Figures

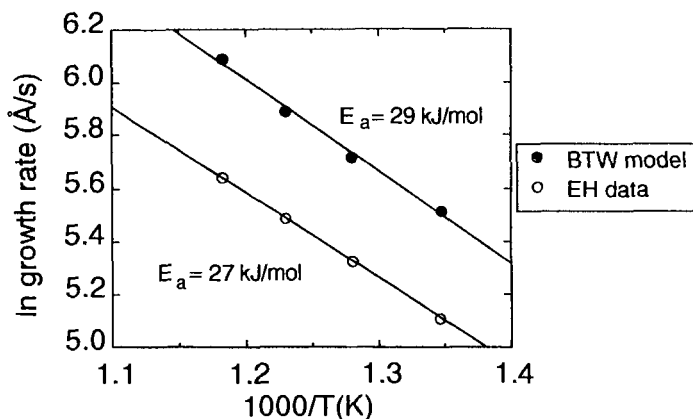


Fig. 1. Arrhenius plot for the peak deposition rate with respect to substrate temperature. Closed circles are model data; open circles experimental data.

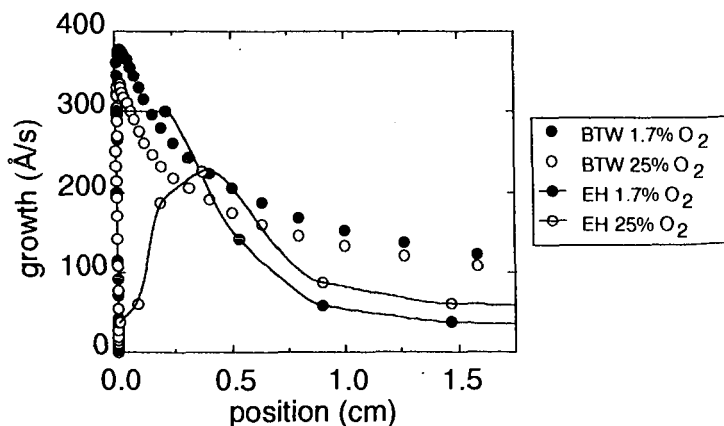


Fig. 2. Model growth profiles under conditions which vary the initial oxygen concentration while keeping the silane concentration constant. Circles without lines are model data; circles with lines are experimental data.

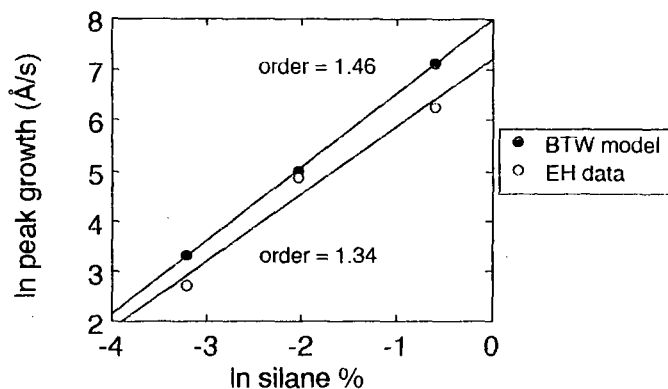


Fig. 3. Plot to determine the order of a possible power law relationship between maximum deposition rate and initial silane mixing ratio. Closed circles are model data; open circles experimental data.

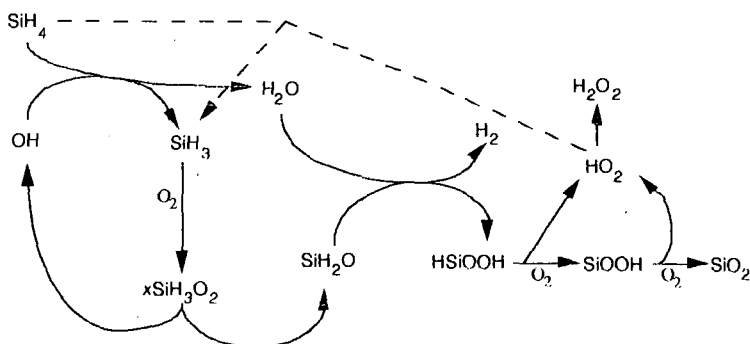


Fig. 4. Major pathways in the BTW mechanism under EH conditions. The solid lines represent primary pathways, and the dashed line branching.